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BIOMIMETIC TRANSALKYLATION OF OLEFINS VIA SULFONIUM SALTS

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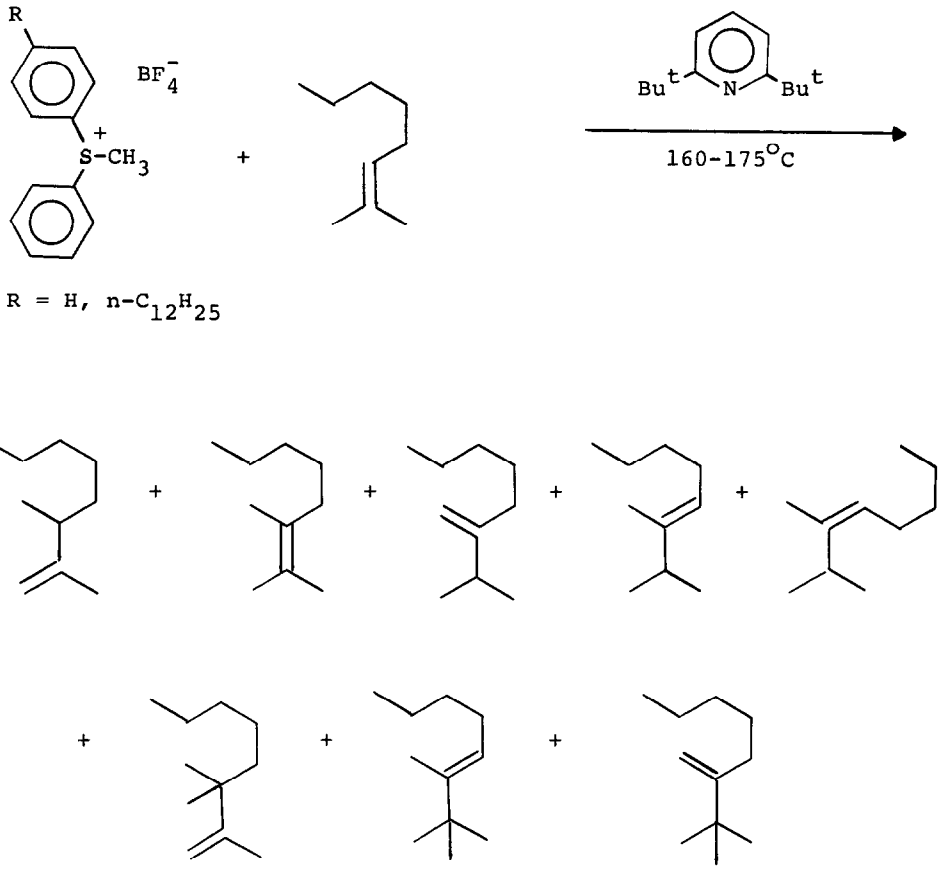
Abstract: The biomimetic transalkylation of 2-methyl-2-octene utilizing alkyl sulfonium salts is discussed in terms of the structure of the salt and the nature of the alkyl group.

The methylation of olefins in many living organisms takes place via a group of methylases which employ as a cofactor S-adenosylmethionine, SAM, a sulfonium salt [1].

Attempts to mimic this biochemical process in the laboratory have yielded encouraging results [2]. Thus it was found that, by employing methyl sulfonium salts, it was possible to transfer a methyl group to the olefin 2-methyl-2-octene (a substrate chosen because of its structural analogy with the Δ^{24} steroid side chain), in overall yields which ranged from 5% to 53%. The reactions were performed in sealed tubes at 160-175°C and required the presence of the non-nucleophilic base di-t-butylpyridine as a proton scavenger. Diarylmethyl sulfonium salts proved more effective than other methylating agents like dimethyl sulfate, methyl trifluoromethanesulfonate or trimethyloxonium fluoroborate. The product consisted of a complex mixture of mono- and dimethylated octenes, presumably formed via methyl addition to the double bond followed by a proton elimination of the intermediate carbocation.



R = H, n-$C_{12}H_{25}$

We have investigated this reaction with the hope of increasing the yields of methylation.

It had been observed that a substantial increase in the yield of methylated products was obtained when a long alkyl chain was grafted onto the para position of one of the rings. We reasoned that, by bringing this alkyl chain closer to the reaction centre, as in compounds (5) below, we might be able to increase the yields of methylation, in agreement with the observation that nucleophilic attack on SAM was facilitated by an active site of low dielectric constant [3].

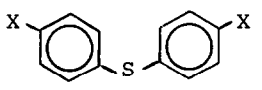
A second alternative was the use of other aromatic sulfonium salts which would generate better sulfide leaving groups. This might be attained by increasing the conjugation of the sulfur atom with the aromatic

rings in more rigid, planar heteroaromatic compounds.

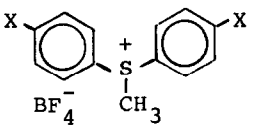
Finally, it would be of interest to exploit sulfonium salts to transfer other alkyl groups to olefinic substrates, hopefully under less drastic conditions than those required for the transmethylation process. We chose as a candidate for these experiments the more labile diphenyl benzyl sulfonium fluoroborate, which might act as an olefin benzylating agent.

Results and Discussion:

A series of diarylmethyl sulfonium fluoroborates (2) and (5) were prepared by reaction of the corresponding sulfides (1) and (4) with trimethyloxonium fluoroborate. Under these conditions the dinitro derivative (1, X = NO_2) and 2,2',4,4'- tetrabromodiphenylsulfide failed to react.



1a: X = Br
1b: X = CH_3



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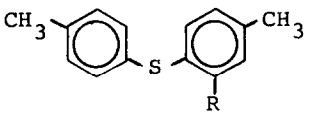
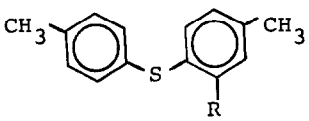
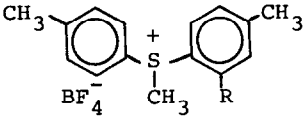


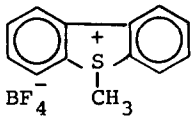
3a: R=CH_3CO
3b: R=$C_5H_{11}CO$
3c: R=$C_8H_{17}CO$
3d: R=$C_{11}H_{23}CO$



4a: R= C_2H_5
4b: R= C_6H_{13}
4c: R= C_9H_{19}
4d: R= $C_{12}H_{25}$



5a: R= C_2H_5
5b: R= C_6H_{13}
5c: R= C_9H_{19}
5d: R= $C_{12}H_{25}$



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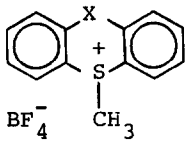
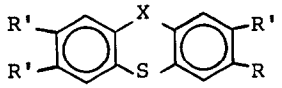
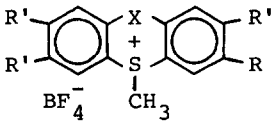


7: X = S
8: X = O



9: X=O,R'=H,R=$C_{11}H_{23}CO$
10: X=O,R'=H,R=$C_{12}H_{25}$
12: X=S,R'=R=OCH_3



11: X=O,R'=H,R=$C_{12}H_{25}$
13: X=S,R'=R=OCH_3

In an analogous way, the sulfonium fluoroborates (6),(7),(8),(11) and (13) were obtained in good yields.

Benzyldiphenyl sulfonium fluoroborate (14) was obtained by reaction of diphenylsulfide and benzyl bromide in the presence of $AgBF_4$, generated *in situ* by treatment of dry Ag_2CO_3 with $HBF_4.Et_2O$.

The reactions of the methyl sulfonium fluoroborates with 2-methyl 2-octene in the presence of di-t-butylpyridine were carried out as described previously [2]. A mixture of mono- (ca. 80%) and dimethylated products was obtained in all cases. The pattern of product distribution was practically the same for all investigated methyl sulfonium fluoroborates, reproducing the distribution previously observed for the reaction of that octene with diphenylmethyl sulfonium fluoroborate [2]. Thus, 2,3-dimethyl-2-octene was always the major product, amounting to about 50% of the mixture. The other most abundant monomethylated products were 2,3-dimethyl-3-octene (ca.15% of the product mixture) and 2,3-dimethyl-1-octene (about 10% of the mixture).

Table 1 gives the total yields of methylated products from salts (2) and (5).

TABLE 1 - Total yield of transmethylation of 2-methyl-2-octene by methyl sulfonium fluoroborates (2) and (5).

Sulfonium Salt	(2a)	(2b)	(5a)	(5b)	(5c)	(5d)
Yield,%	26,27[a]	11,15[a]	24	43	33	42

a) Two runs performed.

As can be seen from the table, the more lipophilic sulfonium salts are more effective as transmethylating agents. Thus, compounds (5b), (5c) and (5d), which have longer alkyl chains attached to the ring, gave higher yields of methylated olefins than compound (2b), a substrate where these chains are absent. The position of the chain is not as important as its size: ortho-substituted diarylsulfonium salts (5) are about as effective as their para-substituted C_{12} analogue[2] in these reactions. These results probably reflect the higher miscibility of the olefinic substrate with salts having a C_6-C_{12} alkyl side chain.

By changing the structure of the sulfonium fluoroborate,we hoped to obtain more reactive and effective transalkylating agents. This could be attained either by changing the nature of the alkyl group to

be transferred, or the structure of the sulfide leaving group.

The first hypothesis was tested by reacting the benzyl sulfonium salt (14) with 2-methyl-2-octene in the presence of di-t-butylpyridine at 160°C for 48 hours. To our disappointment, the analysis by coupled gas chromatography-mass spectrometry of the complex mixture of products revealed less than 2 % of the supposed transbenzylated olefins of mass 216. Our failure was due to the fact that compound (14) was too reactive: when heated at 90°C it decomposed to a mixture of products that consisted of diphenyl sulfide, together with mono- and dibenzylated derivatives of $(C_6H_5)_2S$. This internal Friedel-Crafts alkylation was responsible for the low yield of presumed olefinic transbenzylation.

This negative result showed that transalkylations of olefins by this method were possible only with sulfonium salts which could stand the high temperatures required by the process without appreciable decomposition.

The stability of the alkyldiaryl sulfonium salts might be associated with the polarity of the $\overset{+}{S}$-alkyl bond. More polarized bonds, where the alkyl group, like benzyl, can readily accomodate a positive charge, should be more labile and, accordingly, less effective in olefin transalkylation, than the $\overset{+}{S}$-Me bond.

This hypothesis was confirmed by the yields reported in Table 2.

TABLE 2- Total yields of transmethylation of 2-methyl-2-octene by various methyl sulfonium fluoroborates. Correlation with the chemical shifts of the $\overset{+}{S}$-Me group in $CDCl_3$.

Sulfonium Salt	(2b)	(6)	(7)	(8)	(11)	(13)
Yield, %	13	12	24	32	35	6
$^1H\ \delta_{\overset{+}{S}-CH_3}$	3.60	3.60	3.30	3.25	3.20	3.20

The development of charge on the methyl group was estimated by the chemical shift of the $\overset{+}{S}$-Me group in the n.m.r. spectra of the salts in $CDCl_3$. It is seen that the total yields of transmethylation increase with the higher shielding of the methyl group. The only exception was compound (13), which proved to be a very poor transmethylating agent. This was probably due to the very low miscibility of this high-melting fluoroborate salt with the olefinic substrate, a factor which severely decreased the yields of these reactions.

A general picture emerges from the above considerations. The crucial point in optimizing the process seems to be the competition of nucleophilic species present in the medium for the alkyl group of the sulfonium fluoroborate. As shown before [2], the hindered pyridine, which acts as a proton scavenger, plays no role in this competition. Reactive alkyldiaryl sulfonium fluoroborates, capable of easy dissociation into a diaryl sulfide and a carbocationic species, undergo internal Friedel-Crafts alkylations of the aromatic rings. This is not observed for the less reactive methyl sulfonium salts. However, in this case, a competition for the $\overset{+}{S}$-Me group is established between the olefin and the fluoride anion, originated from the thermal dissociation of the BF_4^- counterion. The harder F^- nucleophile is increasingly favored in methyl displacements from less lipophilic salts, or where the $\overset{+}{S}$-methyl group is more deshielded and, therefore, harder.

The original goal of these investigations was to improve the yield of olefinic transmethylation of this biomimetic process. Our results are, in this respect, disappointing. However, they contribute to a better understanding of this interesting process, which represents one of the few examples of such conversions in the laboratory [4]. The difficulties encountered by us can only underline the remarkable ease and specificity of the biochemical process, which utilizes, according to our standards, an even less reactive trialkylsulfonium salt for the same purpose.

Experimental:

Melting points were taken with a Büchi 510 apparatus and were not corrected. Ir spectra were recorded on a Perkin-Elmer 599 spectrophotometer, nmr spectra on a Cameca 250 MHz model, using tetramethylsilane as internal standard. Mass spectra were obtained with a R-1010 Nermag spectrometer. Chromatographic analyses of the products of the transmethylation reactions were performed on a Girdel 30 gas chromatograph, equipped with a capillary column SE-52 and a Hewlett-Packard integrator. In the separation of the products of reactions a Carlo Erba 4200 preparative gas chromatograph, with a Chromosorb column AW-DMC5 60-80, and a Analprep EC 93 high-pressure liquid chromatograph were also employed.

The following compounds were prepared by methods reported in the literature:

4,4'-Dibromodiphenylsulfide , mp 111°C, lit.[5] 112.4°C; 2,2',4,4'-tetrabromodiphenylsulfide, mp 72°C, lit.[6] 71-73°C; 4,4'-dinitrodiphenylsulfide, mp 159°C, lit. [7] 158-161°C ; 4,4'-dimethyldiphenylsulfide, mp 55°C, lit. [8] 56-57°C ; 2-acetyl-4,4'-dimethyldiphenylsulfide (3a), mp 118°C, lit. [9] 119.5-120°C ; 5-methyldibenzothiophenium fluoroborate (6), mp 148°C, lit. [10] 149-151°C ; thianthrene, mp 157°C, lit. [11] 158-159°C ; phenoxathiin , mp 55°C, lit. [12] 56-57°C; 2-dodecanoylphenoxathiin (9), mp 64-65°C, lit. [14] 68-69°C ; 2,3,7,8-tetramethoxythianthrene (12), mp 174°C, lit. [15] 176°C.

Preparation of 2-Acyl-4,4'-dimethyldiphenylsulfides (3). General Procedure - To a cooled (0°C) stirred solution of 4,4' -dimethyldiphenylsulfide (4.3 g, 2 mmol) in the corresponding acyl chloride (10 mmol) $AlCl_3$ (5.2 g, 4 mmol) was added portionwise during 2-3 minutes. The mixture was then stirred for further 20-30 minutes at 5-10°C , and was then quenched by careful addition of cold water (70 ml).The resulting two-phase system was stirred vigorously and heated at 50-60°C for 1-2 hours, until the excess acyl choride had been hydrolysed. It was then extracted with ether (100 ml) and washed exhaustively with a 2 M NaOH solution, until no more sodium carboxylate was formed, then with a 1 M HCl solution, and finally with water. The ethereal extract was then dried over $CaCl_2$ and the solvent eliminated in a rotary evaporator The oily residue was then triturated with cold methanol, until the solid product separated, or was purified by flash chromatography on silica 60H (Merck).

In such a way the following acylsulfides (3) were prepared:

2-Hexanoyl-4,4'-dimethyldiphenylsulfide (3b) - 74% yield, mp 46-48°C (Found C, 76.72; H, 7.88; S, 10.13%. $C_{20}H_{24}SO$ requires C, 76.92; H, 7.96; S, 10.26%). $\bar{\nu}_{max}$ (nujol) 1660, 1180 and 810 cm^{-1}; δ ($CDCl_3$) 0.9 (3H, m); 1.4 (4H,m); 1.8 (2H,m); 2.35 (3H,s); 2.4 (3H,s);3.0 (2H, t,J 7 Hz); 6.9 (1H, d,J 8 Hz); 7.1 (1H, d, J 8 Hz); 7.2 (2H,d, J 8Hz); 7.4 (2H,d,J 8 Hz) and 7.6 (1H,s).

2-Nonanoyl-4,4'dimethyldiphenylsulfide (3c) - purified by flash chromatography, pentane as eluent, yield 45%, mp 32-33°C (from cold MeOH) (Found C, 77.88; H, 8.51; S, 8.84%. $C_{23}H_{30}SO$ requires C, 77.96; H, 8.47; S, 9.04%). $\bar{\nu}_{max}$(KBr) 2910, 2840, 1670, 1460 and 810 cm^{-1} ; δ ($CDCl_3$) 0.9 (3H,m); 1.3 (10H, m); 1.8 (2H,m); 2.35(3H,s); 2.4(3H, s); 3.0 (2H,t,J 7 Hz); 6.9 (1H,d,J 8 Hz); 7.1 (1H,d,J 8 Hz); 7.2 (2H, d,J 8 Hz); 7.4 (2H, d,J 8 Hz) and 7.6 (1H,s).

2-Dodecanoyl-4,4'-dimethyldiphenylsulfide (3d) - 66% yield,mp 69-71°C (from MeOH) (Found C, 78.93; H, 9.25; S, 8.10%.$C_{26}H_{36}SO$ requires C, 78.79; H, 9.09; S, 8.08%). $\bar{\nu}_{max}$(nujol) 1660,810 cm^{-1}; δ ($CDCl_3$) 0.9 (3H,m); 1.3(16H,m); 1.8(2H,m); 2.35(3H,s); 2.4(3H,s); 3.0 (2H, t,J7Hz) 6.9 (1H,d,J 8 Hz); 7.1 (1H,d,J 8 Hz); 7.2 (2H,d,J 8 Hz); 7.4(2H,d,J8Hz) 7.6 (1H,s).

Reduction of ketones (3) and (9). General Procedure -To a stirred and cooled (0°C) suspension of $AlCl_3$ (2.6 g, 20 mmol) and $LiAlH_4$ (0.5 g, ca 12 mmol) in dry THF (30 ml), a solution of the ketone (3.0 mmol) and $AlCl_3$ (2.6 g,20 mmol) in dry THF (30 ml) was added dropwise. The mixture was then stirred at 25°C for 30 minutes and then refluxed for 6-12 h, until the reaction was over, as shown by thin-layer chromatography. The excess $LiAlH_4/AlCl_3$ was then quenched with cold water (10 ml), the resulting mixture poured into 100 ml of a 0.1 N HCl solution , and extracted with ether (70 ml). The ethereal layer was washed with water, dried over $CaCl_2$ and rotary-evaporated. The crude product was purified by flash-chromatography, using pentane as eluent.

The following sulfides were prepared in this way:

2-Ethyl-4,4'-dimethyldiphenylsulfide (4a) - colorless oil,95% yield (Found C, 79.42; H, 7.47; S, 13.04%. $C_{16}H_{18}S$ requires C, 79.34; H, 7.44; S, 13.22%). $\bar{\nu}_{max}$(neat) 2940, 2920, 1490, 1460 and 800 cm^{-1}; δ ($CDCl_3$) 1.2 (3H,t,J 7 Hz); 2.25(3H,s) 2.3(3H,s); 2.75(2H,q,J 7Hz);7.0-7.2(7H,m)

2-Hexyl-4,4'-dimethyldiphenylsulfide (4b) -colorless oil, 82% yield (Found C, 80.63; H, 8.82; S, 10.55%. $C_{20}H_{26}S$ requires C, 80.54; H, 8.72; S, 10.74%). $\bar{\nu}_{max}$(neat) 2940, 2920,2840,1490 and 800 cm^{-1}; δ ($CDCl_3$) 0.9 (3H,m); 1.35(6H,m); 1.5(2H,m); 2.25(3H,s); 2.3(3H,s); 2.75(2H,t,J 7Hz); 7.0-7.2(7H,m).

2-Nonyl-4,4'-dimethyldiphenylsulfide (4c) -colorless oil, 75% yield (Found C, 81.26; H, 9.57; S, 9.21%. $C_{23}H_{32}S$ requires C, 81.18; H, 9.41; S, 9.41%). $\bar{\nu}_{max}$ (neat) 2920, 2840,1490 and 800 cm^{-1}; δ ($CDCl_3$)0.9(3H,m) 1.35 (12H,m); 1.5 (2H,m); 2.25(3H,s); 2.3(3H,s); 2.75(2H,t,J 7 Hz); 7.0-7.2 (7H,m).

2-Dodecyl-4,4'-dimethyldiphenylsulfide (4d)-colorless oil,70% yield (Found C, 81.56; H, 9.93; S, 8.18%. $C_{26}H_{38}S$ requires C, 81.68; H, 9.95; S, 8.38%). $\bar{\nu}_{max}$(neat) 2920, 2840, 1490 and 800 cm^{-1}; δ ($CDCl_3$) 0.9(3H, m); 1.35(18H,m); 1.5(2H,m); 2.25(3H,s); 2.3(3H,s); 2.75(2H,t,J 7Hz);7.0-7.2(7H,m).

2-Dodecylphenoxathiin (10) - colorless oil, 86% yield (Found C,78.11 H,8.67; S,8.50%. $C_{24}H_{32}OS$ requires C, 78.26; H,8.70; S, 8.70%). $\bar{\nu}_{max}$ (neat) 2920, 2850, 1460, 1260, 1230 and 750 cm^{-1}; δ ($CDCl_3$) 0.9(3H,m); 1.25 (18H,m); 1.4(2H,m); 2.5(2H,t,J 7Hz); 6.9-7.1(7H,m).

Preparation of Methylsulfonium Fluoroborates (2), (5), (7), (8), (11) and (13). General Procedure - A suspension of trimethyloxonium fluoroborate (0.44 g, ca 3 mmol) and the sulfide (2 mmol) in $CHCl_3$ (50 ml) was refluxed until the latter reagent had been consumed, as shown by t.l.c.(ca 10 h). The resulting solution was then washed with water (50 ml),dried over anhydrous $CaCl_2$ and evaporated. The crude product was purified by dissolving the residue in acetone and reprecipitating with ether. In the case of oily sulfonium salts, the viscous products were dried for 2-3 days under vacuum; in many cases, after several days these dry waxy compounds solidified.

The following fluoroborates were prepared in this way:

Bis(4-bromophenyl)methylsulfonium fluoroborate (2a) - crystals, mp 109-111°C (from acetone/ether), 85% yield (Found C, 34.83 ; H , 2.59 %. $C_{13}H_{11}Br_2BF_4S$ requires C, 34.98; H, 2.47%). $\bar{\nu}_{max}$(nujol) 1050 and 810 cm^{-1} δ ($(CD_3)_2CO$) 4.0(3H,s); 8.0(4H,d,J 9 Hz); 8.15(4H,d,J 9 Hz).

Bis(4-methylphenyl)methylsulfonium fluoroborate (2b)- solid, mp 78-81°C, 93% yield (Found C, 57.00; H, 5.41; S, 10.27%. $C_{15}H_{17}BF_4S$ requires C,56.96; H,5.38; S,10.13%). $\bar{\nu}_{max}$(nujol) 1050,920 and 810 cm^{-1}; δ ($CDCl_3$) 2.3(6H,s); 3.6(3H,s); 7.3(4H,d,J 8Hz); 7.75(4H,d,J 8Hz).

2-Ethyl-4-methylphenyl-(4-methylphenyl)methylsulfonium fluoroborate (5a) - solid, mp 110-113°C, 75% yield (Found C, 59.32; H, 6.22; S, 9.11%. $C_{17}H_{21}BF_4S$ requires C,59.30; H,6.10; S,9.30%). $\bar{\nu}_{max}$(nujol) 1050 cm^{-1}; δ ($CDCl_3$) 1.7(3H,t,J 7 Hz); 2.4(6H,s); 2.8(2H,q,J 7 Hz); 3.55(3H,s); 7.3(1H, s); 7.45(3H,d,J 8 Hz); 7.8(2H,d,J 8Hz); 8.0(1H,d,J 8 Hz).

2-Hexyl-4-methylphenyl-(4-methylphenyl)methylsulfonium fluoroborate (5b) - wax, 71% yield (Found C, 62.99; H,7.38; S,8.17%. $C_{21}H_{29}BF_4S$ requires C, 63.00; H,7.25; S,8.00%). $\bar{\nu}_{max}$(nujol) 1050 cm^{-1}; δ ($CDCl_3$) 0.8(3H,m); 1.2(8H,m); 2.4(6H,s); 2.8(2H,m); 3.55(3H,s); 7.3(1H,s); 7.45(3H,d, J 8Hz); 7.8(2H,d,J 8Hz); 8.0(1H,d,J 8Hz).

2-Nonyl-4-methylphenyl(4-methylphenyl)methylsulfonium fluoroborate (5c) - wax, 66% yield (Found C, 65.06; H,8.10; S,7.40%.$C_{24}H_{35}BF_4S$ requires C, 65.15; H, 7.92; S,7.24%). $\bar{\nu}_{max}$(nujol) 1050 cm^{-1}; δ ($CDCl_3$) 0.8(3H,m); 1.2(14H,m); 2.4(6H,s);2.8(2H,m); 3.55(3H,s); 7.3(1H,s); 7.45 (3H,d,J 8Hz); 7.8(2H,d,J 8 Hz); 8.0(1H,d,J 8Hz).

2-Dodecyl-4-methylphenyl-(4-methylphenyl)methylsulfonium fluoroborate (5d) - wax, 78% yield (Found C,66.90; H,8.41; S,6.43%. $C_{27}H_{41}BF_4S$ requires C,66.94; H,8.47; S,6.61%). $\bar{\nu}_{max}$(nujol) 1050 cm^{-1}; δ ($CDCl_3$)0.8(3H,m); 1.2 (20H,m); 2.4(6H,s); 2.8(2H,m); 3.55(3H,s); 7.3(1H,s),7.45(3H,d,J 8Hz); 7.8 (2H,d,J 8Hz); 8.0(1H,d,J 8Hz).

2-Methylthianthrenium fluoroborate (7) - crystals, mp 188-190°C (acetone/ether), 70% yield (Found C,48.89; H,3.28; S,20.05%. $C_{13}H_{11}BF_4S_2$ requires C,49.06; H,3.46; S,20.12%). $\bar{\nu}_{max}$(nujol) 1050 and 760 cm^{-1}; δ ($CDCl_3$) 3.3(3H,s); 7.7-7-9(4H,m); 8.4(4H,dd,J 8Hz and 1 Hz).

10-Methylphenoxathiinium fluoroborate (8) - crystals, mp 201-203°C (acetone/ether), 67% yield (Found C, 51.58; H,3.79; S,10.76%.$C_{13}H_{11}BF_4SO$ requires C, 51.56; H,3.64; S,10.60%). $\bar{\nu}_{max}$(nujol) 1450, 1270, 1070,1030, 880 and 770 cm^{-1}; δ ($CDCl_3$) 3.25(3H,s); 7.6(4H,m); 7.85(2H,m); 8.2(2H,dd, J 8Hz and 1 Hz).

2-Dodecyl-10-methylphenoxathiinium fluoroborate (11)- solid, mp 59-61°C, 70% yield (Found C,63.64; H,7.60; S,6.64%. $C_{25}H_{35}BF_4OS$ requires C,63.83; H,7.45; S,6.81%). $\bar{\nu}_{max}$(KBr) 2920,1460 and 1050 cm^{-1}; δ ($CDCl_3$) 0.8(3H,m); 1.2(18H,m); 1.6(2H,m); 2.75(2H,m); 3.2(3H,s); 7.5-7.6(4H,m); 7.8-8.2(3H,m)

5-Methyl-2,3,7,8-tetramethoxythianthrenium fluoroborate(13)-crystals mp 257-259°C (acetone/ether), 72% yield (Found C,46.53; H,4.35;S,14.51%. $C_{17}H_{19}BF_4O_4S_2$ requires C,46.58; H,4.34; S,14.61%). $\bar{\nu}_{max}$(KBr) 1490,1260, 1220,1050, and 1020 cm^{-1}; δ ($CDCl_3$) 3.2(3H,s); 4.0(6H,s); 4.05 (6H,s); 7.2(2H,s); 7.8(2H,s).

Transmethylation Reactions. General Procedure - A mixture of the methylsulfonium fluoroborate (1 molar equivalent), 2-methyl-2-octene(1.5 eq.), 2,6-di-t-butylpyridine (1.2 eq.) and the reference n-undecane (0.2 eq.) was heated for 48 h at 160-175°C in a sealed tube. The products were then analysed by capillary g.c. (initial temperature of the column 50°C, rate of temperature increase 3°C/min). Under these conditions the monomethylated olefins had retention times of 7.05, 7.26, 7.46 and 8.68 min, and the dimethylated octenes of 9.39 and 9.47 minutes.

The total yields of transmethylation for all sulfonium salts prepared are listed in Tables 1 and 2.

Benzyldiphenylsulfonium fluoroborate (14) - To a stirred solution of $HBF_4.Et_2O$ (5g, 30.9 mmol, 4.3ml) in CH_2Cl_2 (5 ml), cooled at 5-10°C, was added dry Ag_2CO_3 [16] (3.4 g, 12.3 mmol). When the CO_2 evolution had subsided, a solution of diphenylsulfide (4 g, 21.5 mmol) in CH_2Cl_2(5 ml) was added, and then benzyl bromide (6.8 g, 40 mmol, 4.8 ml) in CH_2Cl_2(10 ml). The mixture was stirred at 25°C for 10-12 h. It was then filtered and the precipitated AgBr washed with dichloromethane. The filtrate was then evaporated and the oily residue washed with pentane and then scratched with ether until the crude product solidified. The fluoroborate was purified by redissolution in dichloromethane, filtration and reprecipi-

tation by the addition of ether. Yield 5.7 g (78%), mp 99°C, mp lit.[17] 102.5°C .

Thermal Decomposition of Benzyldiphenylsulfonium Fluoroborate (14)

In a stoppered round-bottomed flask the salt (14) (1 g) was heated at 90°C for 4 h, the flask being occasionally opened to release pressure. The resulting viscous mass was extracted with ether and the ethereal extract evaporated to give an oily residue which weighed 480 mg. Gas chromatographic analysis of the oil showed that the mixture consisted of diphenylsulfide and other heavier products, with no traces of benzyl fluoride.

The oil was then separated into three fractions by flash chromatography using pentane as eluent, and each fraction separated into its major components by preparative h.p.l.c., using n-octane as eluent. The three major products detected in the gas chromatograph were thus identified by their mass and pmr spectra as the three isomeric benzyldiphenyl sulfides: 2-benzyldiphenylsulfide, t_r = 6.54 min; δ ($CDCl_3$) 4.1(2H,s); 7.2-7.4(14H,m). M/e 276, 197(major, $C_{13}H_9S^{+\cdot}$, dibenzopyrylium radical cation), 165 ($C_{13}H_9^{+\cdot}$, fluorenium radical cation), 152 ($C_{12}H_8^{+\cdot}$),91 and 77. 3-Benzyldiphenylsulfide, t_r= 7.96 min; δ ($CDCl_3$) 4.2(2H,s); 7.2-7.4(14H,m). M/e 276 (major), 199 ($M^{+\cdot} - C_6H_5$), 167 ($M^{+\cdot} - C_6H_5S$), 165, 152, 91 and 77. 4-Benzyldiphenylsulfide, t_r= 9.52 min ; δ ($CDCl_3$) 4.0 (2H,s); 7.2-7.4(14H,m). M/e 276, 199, 167, 165(major), 152, 91 and 77.

In addition , a heavier fraction was isolated, which consisted of a mixture of products of dibenzylation of diphenylsulfide, as shown by its mass spectrum, m/e 366, 275 ($M^{+\cdot} - C_6H_5CH_2$), 167, 165(major) and 91.

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